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IRON ORES - DETERMINATION OF WATER SOLUBLE CHLORIDE - ION-SELECTIVE ELECTRODE METHOD

STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA STAGE A - 1982

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Extractive Metallurgy Laboratory

January 1983

(For submission to the ISO/TC 102/SC 2/WG 22 A and to the Secretariat of ISO/TC 102/SC 2)

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IRON ORES - DETERMINATION OF WATER SOLUBLE CHLORIDE - ION-SELECTIVE ELECTRODE METHOD STATISTICAL EVALUATION OF INTERNATIONAL TEST DATA - 1982

by

R. Sutarno* and W.S. Bowman**

SUMMARY

The analytical data collected from the international test conducted by ISO/TC 102/SC 2/WG 22 A, on the determination of water soluble chloride content in iron ores by the ion-selective electrode method, during the period of 1980-1982 have been statistically evaluated to estimate the precision of the method.

It was found that the preliminary precision can be expressed in terms of the chloride content in the sample by the following linear equations:

$$r = 0.0861\ X + 0.0017$$
$$P = 0.2969\ X - 0.0078$$
$$\sigma_r = 0.0304\ X + 0.0006$$
$$\sigma_L = 0.1028\ X - 0.0031$$

where r is the repeatability, P is the permissible tolerance, σ_r is the within-laboratory standard deviation, σ_L is the between-laboratories standard deviation and X is the water soluble chloride content in the sample, all expressed in per cent.

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ISO/TC 102/SC 2/WG 22A (WG 12-10)

Janvier 1983

MINÉRAIS DE FER - DOSAGE DES CHLORURES SOLUBLES DANS L'EAU - ÉVALUATION STATISTIQUE DES DONNÉES D'ESSAIS INTERNATIONAUX OBTENUES PAR LA MÉTHODE DE L'ÉLECTRODE SPÉCIFIQUE

par

R. Sutarno* et W.S. Bowman**

RÉSUMÉ

Les données analytiques recueillies lors des essais internationaux effectués par ISO/TC 102/SC 2/WG 22A sur le dosage des chlorures solubles dans l'eau par la méthode de l'électrode spécifique pendant la période 1980-1982, ont été évaluées statistiquement dans le but d'estimer la précision de la méthode.

Les premières estimations de la précision peuvent être exprimées en fonction de la concentration en chlorures dans l'échantillon par les équations suivantes:

$$r = 0,0861\ X + 0,0017$$
$$P = 0,2969\ X - 0,0078$$
$$\sigma_r = 0,0304\ X + 0,0006$$
$$\sigma_L = 0,1028\ X - 0,0031$$

où r est la répétabilité, P est la tolérance admissible, σ_r est l'écart-type à l'intérieur d'un laboratoire, σ_L est l'écart-type entre les laboratoires et X est la concentration en chlorures solubles dans l'eau, toutes exprimées en pour cent.

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INTRODUCTION

The development of a standard method for the determination of water soluble chloride content in iron ores was one of the new work items introduced at the tenth meeting of ISO/TC 102/SC 2 (Resolution 37 - Pretoria 1980)[1]. A working group (WG 22 A) was formed to undertake this task.

During the period of 1980-1982, WG 22 A conducted a preliminary international test. Four samples with water soluble chloride contents ranging from 0.08 to 0.9% were used. Fourteen laboratories participated in the international test; each analyzed the samples in triplicate. The results of this international test were discussed at the eleventh meeting of the sub-committee. It was decided that further development of the method is still necessary and the working group mandate was extended at stage A[2] for another two years (Resolution 25 - Ottawa 1982). The purpose of this statistical evaluation is to provide a rough estimate of the precision of the analytical method at the present stage; it will be compared with the precision of the method in the future when it has been further developed.

PRINCIPLE OF THE ANALYTICAL METHOD[3]

The test portion is digested in water and the suspension transferred to a volumetric flask and diluted to volume. After dry filtration, an aliquot is treated with potassium persulphate solution and ionic strength adjuster solution is added. Chloride concentration is determined potentiometrically using a chloride ion electrode and double junction reference electrode.

STATISTICAL EVALUATION

The data were statistically evaluated in accordance with the procedure described in document ISO/TC 102/SC 2 (WG 7-21) N 532 E[4] and schematically illustrated in Figure 1. The factor 2.77 used for conversion of standard deviations to their respective expressions of precisions has been replaced by 2.83. The data are also plotted in Figure 2. The boxed points in Figure 2 signify that these data were suspected outliers and were excluded from computation of grand means and precisions; the reasons for this are explained in the detailed computation presented in Appendix A. The results

of this computation are presented in Table 1. Linear regression lines between the precisions and their corresponding grand means are presented in Figure 3.

OBSERVATIONS

Contrary to the many difficulties reportedly experienced by various laboratories[2], from the statistical point of view, the results of this international test are encouraging. Table 1 shows that the precision is generally acceptable for this stage of development. Table 2 shows that the σ_L/σ_r ratios are acceptable with the exception of sample 82-4. Furthermore, only two laboratories reported outliers. This usually indicates that the difficulties in applying the analytical method are not serious, although there seems to be room for improvement in the precision.

ABBREVIATIONS USED IN THIS REPORT

σ_r = SIGMA-R - within-laboratory standard deviation

σ_L = SIGMA-L - between-laboratories standard deviation

r* = R-repeatability
= 2.83 σ_r

P** = permissible tolerance between laboratories

$$= 2.83 \sqrt{\sigma_L^2 + \sigma_r^2/2}$$

COUNTRY ABBREVIATIONS

AU = Australia
JP = Japan
SW = Sweden
NL = Netherlands

* Repeatability, r, is the value below which the absolute difference between two independent single test (analysis) results produced by a laboratory on identical material using the same equipment within a short interval of time, using the standardized test method, may be expected to lie with a 95% probability.

** Permissible tolerance between laboratories, P, is the value below which the absolute difference between two means of duplicate test results on identical material obtained by operators of different laboratories using the standardized test method, may be expected to lie with a 95% probability.

REFERENCES

1. "Final Report of the Tenth Meeting of ISO/TC 102/SC 2 - Iron Ores/ Chemical Analysis", ISO/TC 102/SC 2 N 655 E, August 1981.

2. "Draft Report of the Eleventh Meeting of ISO/TC 102/SC 2 - Iron Ores/ Chemical Analysis", ISO/TC 102/SC 2 N 720 E, November 1982.

3. "Iron Ores - Determination of Water Soluble Chloride Content - Ion Selective Electrode Method", ISO/TC 102/SC 2 (WG 22 A-5) N 688 E, August 1982.

4. "Procedure for Statistical Evaluation of Analytical Data Resulting from International Tests", ISO/TC 102/SC 2 (WG 7-21) N 532 E, August 1978.

Table 1

ISO/TC 102/SC 2/WG 22 A - Water Soluble Chloride

SUMMARY OF PRECISIONS FOR ALL SAMPLES

SAMPLE	MEAN(X)	REPEATABILITY	PERMISSIBLE TOLERANCE	SIGMA-R	SIGMA-L
82-1	.0076	.0010	.0023	.00037	.00077
82-2	.0137	.0033	.0040	.00117	.00114
82-3	.1760	.0181	.0254	.00640	.00773
82-4	.9078	.0797	.2652	.02815	.09158

THE REGRESSION EQUATIONS ARE:						CORR. COEFF.
r	=	.0861	X	+	.0017	.9996
P	=	.2969	X	-	.0078	.9949
SIGMA-R	=	.0304	X	+	.0006	.9996
SIGMA-L	=	.1028	X	-	.0031	.9939

Table 2 - List of outliers and ratio of the between laboratories standard deviation σ_L to the within laboratories standard deviation σ_r

Sample	Mean X	K_o	N_o	K	N	Outliers			σ_L/σ_r
						Cochran (precision)	Dixon (accuracy)	Individual result	
82-1	0.0076	14	42	14	42	-	---	---	2.1
82-2	0.0137	14	42	13	39	-	AU 3	---	1.0
82-3	0.1760	14	42	13	39	-	AU 3	---	1.2
82-4	0.9078	14	42	13	39	-	JP 2	---	3.4

k_o - total number of participating laboratories
k - number of sets of laboratory results used for estimating precision
N_o - total number of results submitted for a particular test sample
N - number of results used for estimating precision

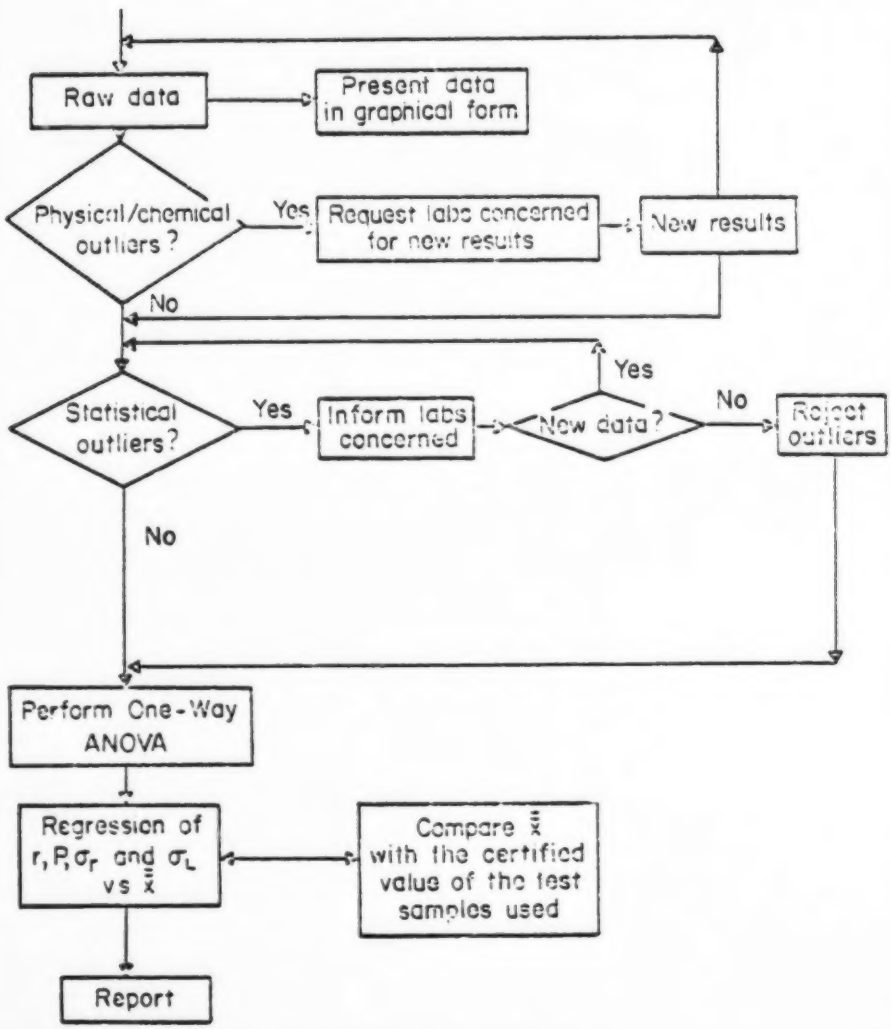

Figure 1. Flow Chart of the Procedure for Statistical Evaluation of Analytical Data Resulting from International Tests.

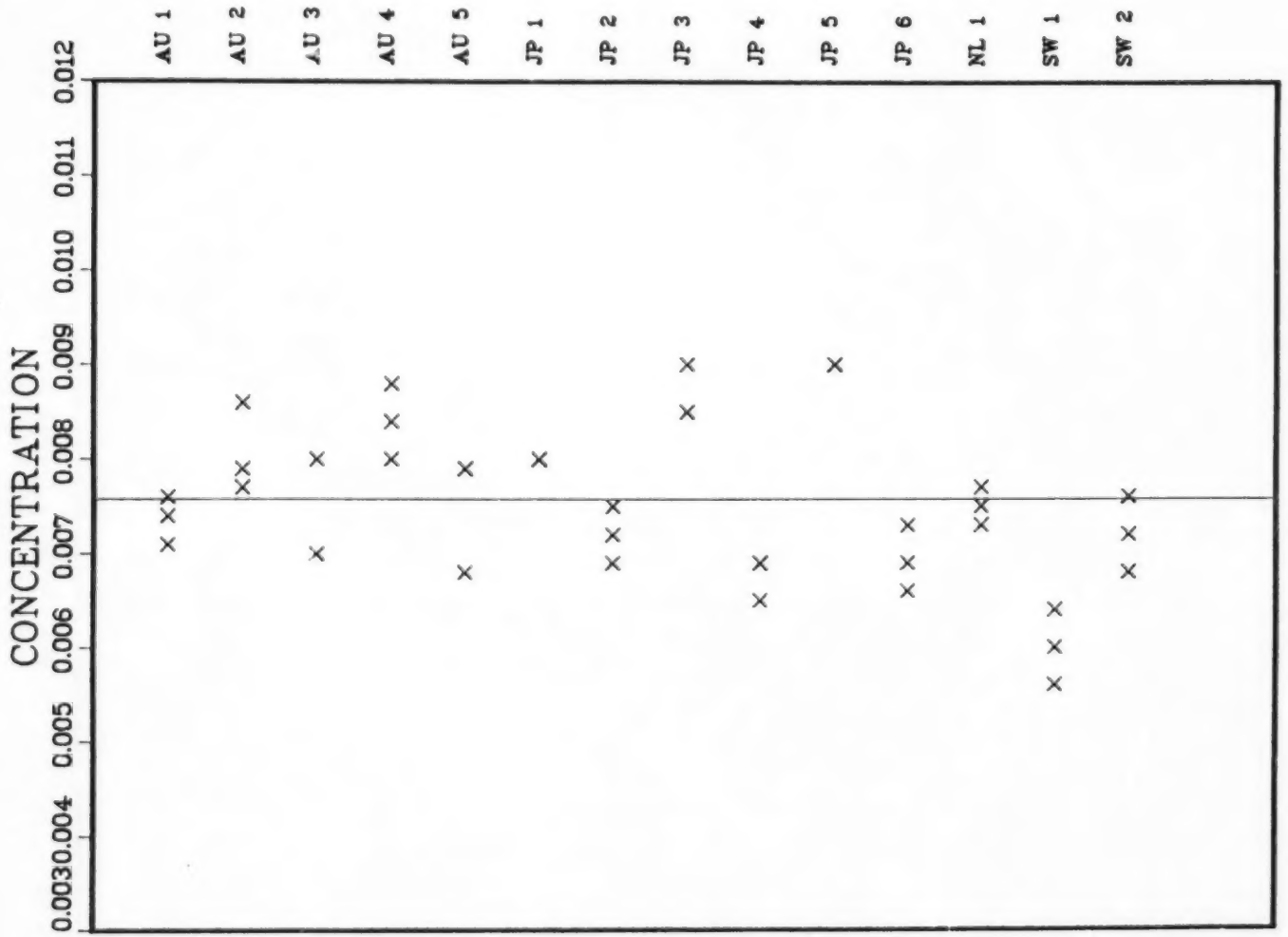

Figure 2.1.

ISO/TC 102/SC 2/WG 22A – WATER SOLUBLE CHLORIDE

SAMPLE: 82–1 (MARRA MAMBA)

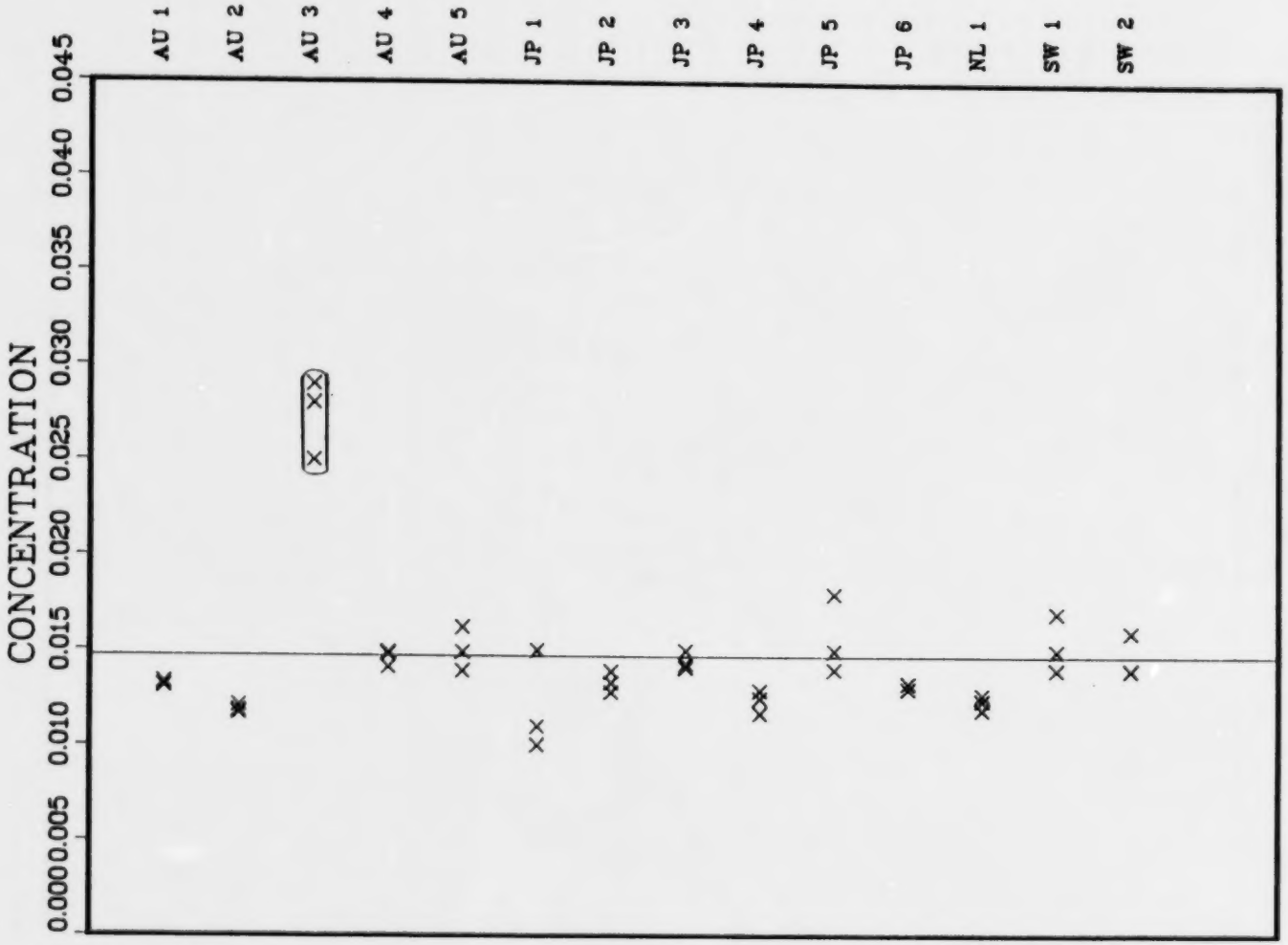

Figure 2.2.

ISO/TC 102/SC 2/WG 22A – WATER SOLUBLE CHLORIDE

SAMPLE: 82-2 (USINOR KDF)

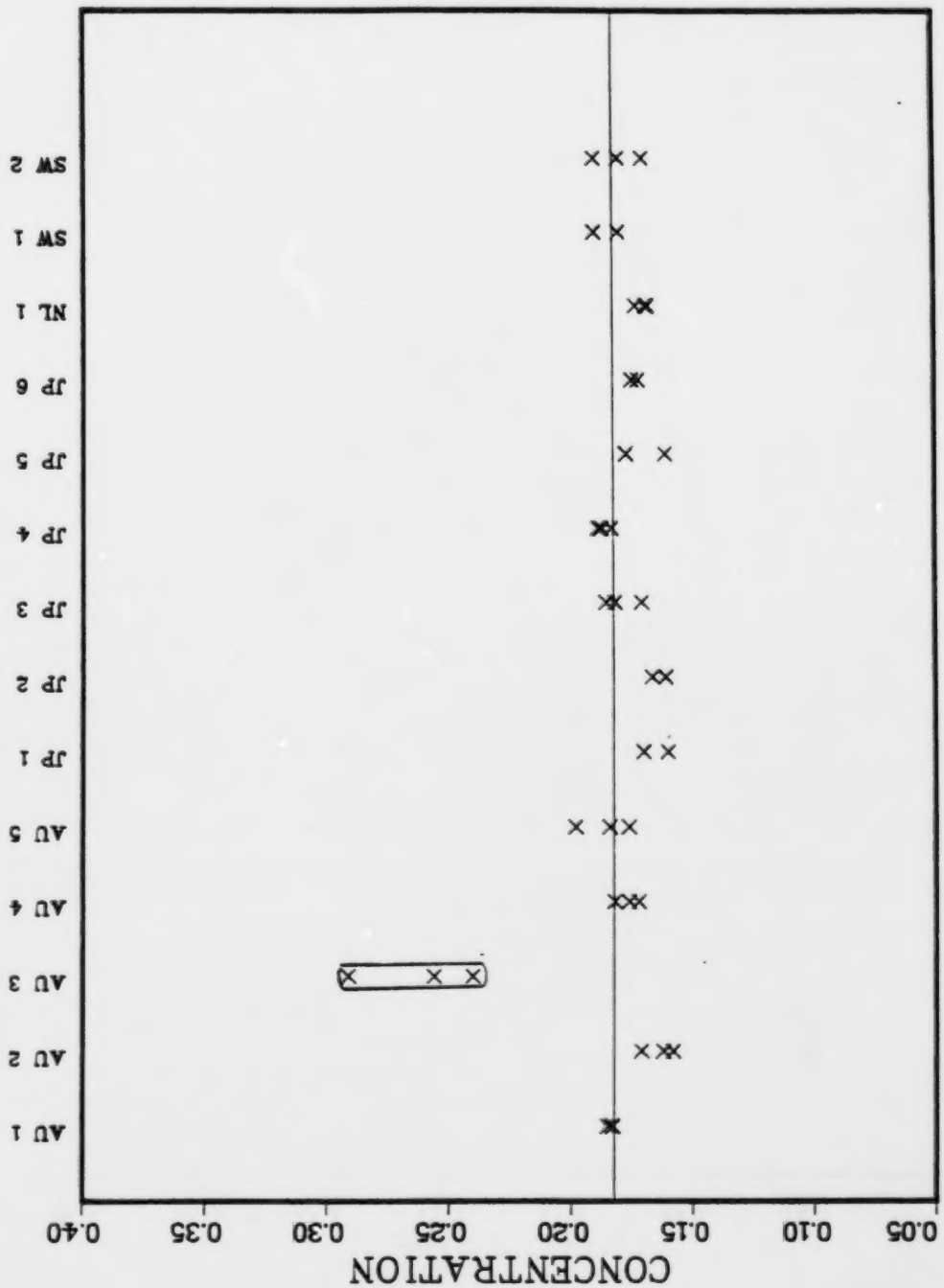

Figure 2.3.
ISO/TC 102/SC 2/WG 22A – WATER SOLUBLE CHLORIDE
SAMPLE: 82-3 (MALMBERGET CONC)

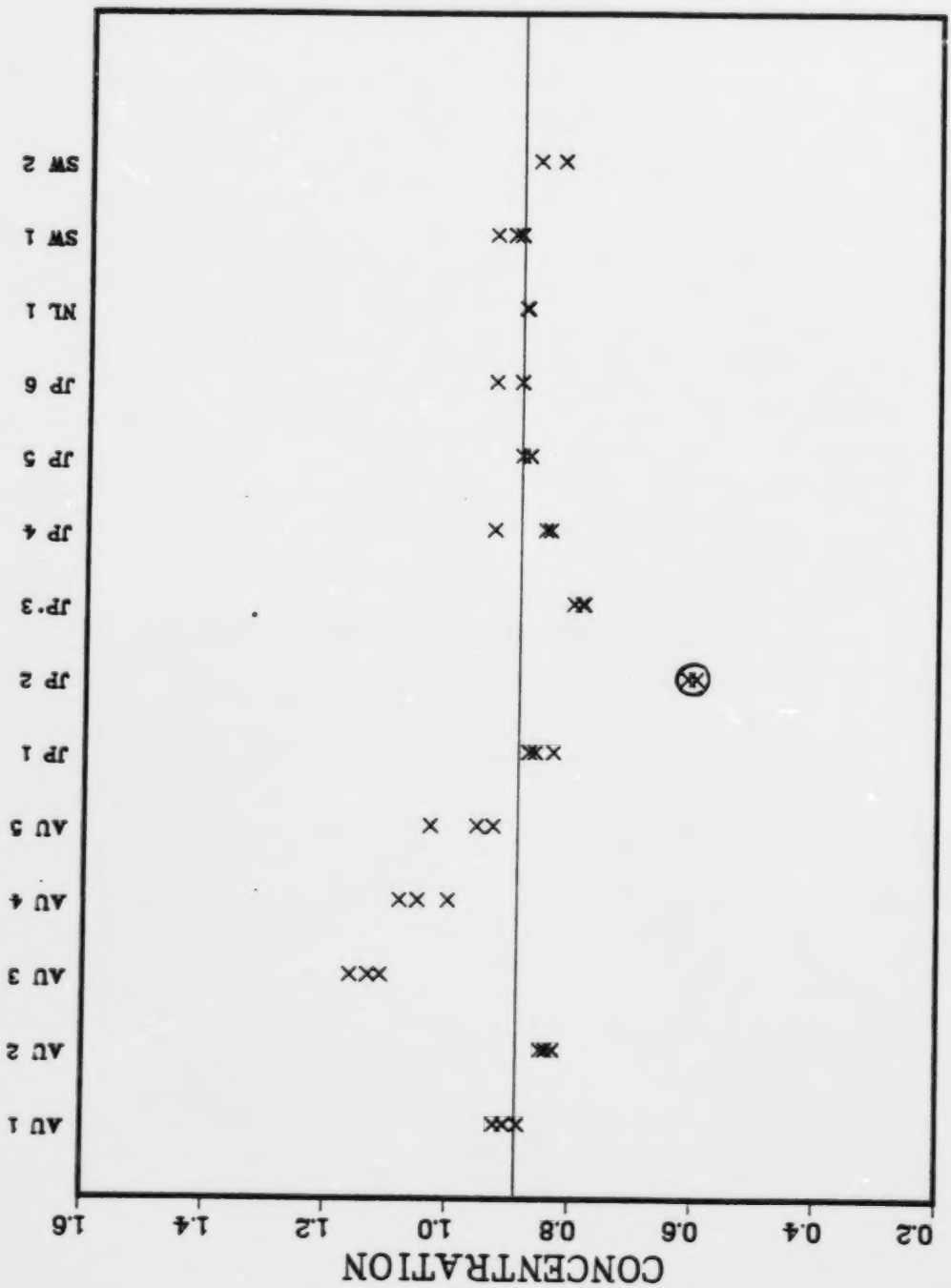

Figure 2.4.
ISO/TC 102/SC 2/WG 22A – WATER SOLUBLE CHLORIDE
SAMPLE 82–4 (MALMBERGET CONC)

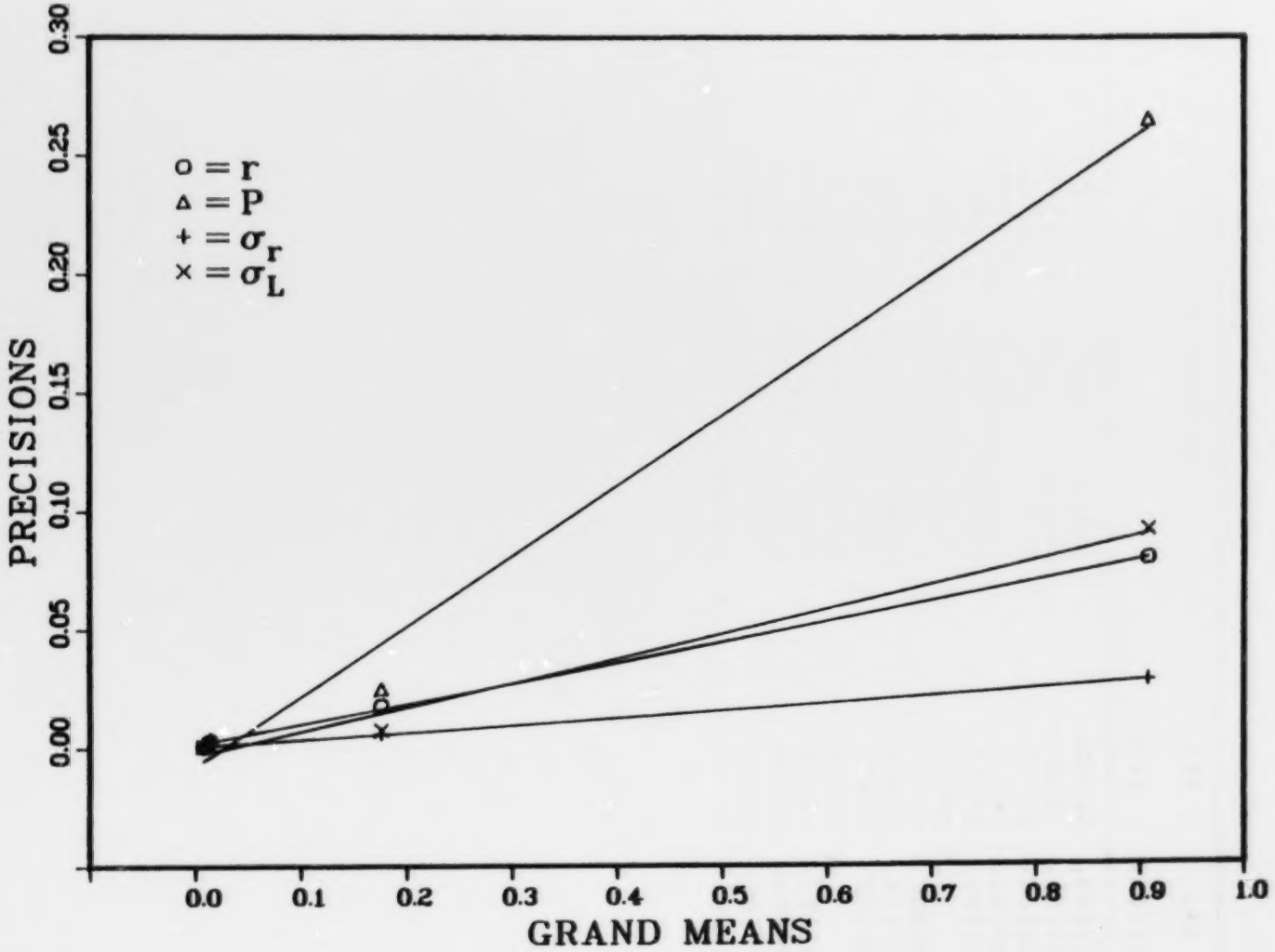

Figure 3
ISO/TC 102/SC 2/WG 22A – WATER SOLUBLE CHLORIDE

APPENDIX A

DETAILED COMPUTATION OF THE ANALYTICAL DATA

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-1 (MARRA MAMBA)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS			LAB MEAN	LAB VARIANCE
1	AU 1	1	.0071	.0076	.0074	.00737	.6333E-07
2	AU 2	1	.0079	.0077	.0086	.00807	.2233E-06
3	AU 3	1	.0070	.0080	.0070	.00733	.3333E-06
4	AU 4	1	.0084	.0080	.0088	.00840	.1600E-06
5	AU 5	1	.0079	.0068	.0079	.00753	.4033E-06
6	JP 1	1	.0080	.0080	.0080	.00800	0.
7	JP 2	1	.0069	.0072	.0075	.00720	.9000E-07
8	JP 3	1	.0085	.0090	.0085	.00867	.8333E-07
9	JP 4	1	.0065	.0069	.0069	.00677	.5333E-07
10	JP 5	1	.0090	.0090	.0090	.00900	0.
11	JP 6	1	.0069	.0066	.0073	.00693	.1233E-06
12	NL 1	1	.0077	.0073	.0075	.00750	.4000E-07
13	SW 1	1	.0056	.0060	.0064	.00600	.1600E-06
14	SW 2	1	.0076	.0072	.0068	.00720	.1600E-06

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-1 (MARRA MAMBA)

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	4.641
CHI-SQUARE(.95,11)	19.681

VARIANCE IS HOMOGENEOUS
(COCHRAN'S TEST NOT PERFORMED)

DIXON'S TEST FOR LABORATORY MEANS

NONE REJECTED

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

ALL RESULTS WERE USED EXCEPT INDIVIDUAL REPLICATES LISTED BELOW

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-1 (MARRA MAMBA)

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	13	.24783095E-04	.19063919E-05
WITHIN LABS	28	.37866667E-05	.13523810E-06
TOTAL	41	.28569762E-04	

REPEATABILITY VARIANCE	.13523810E-06
REPEATABILITY STD. DEV.	.00036775
BETWEEN-LABORATORIES VARIANCE	.59038462E-06
BETWEEN-LABORATORIES STD. DEV.	.00076836
REPEATABILITY	.00104072
PERMISSIBLE TOLERANCE BETWEEN LABS	.00229562
GRAND MEAN	.00756905
VARIANCE OF THE GRAND MEAN	.45390284E-07

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-2 (USINOR KDF)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS			LAB MEAN	LAB VARIANCE
1	AU 1	1	.0131	.0133	.0133	.01323	.1333E-07
2	AU 2	1	.0117	.0118	.0121	.01187	.4333E-07
3	AU 3	1	.0280	.0250	.0290	.02733	.4333E-05
4	AU 4	1	.0148	.0141	.0149	.01460	.1900E-06
5	AU 5	1	.0149	.0162	.0139	.01500	.1330E-05
6	JP 1	1	.0100	.0110	.0150	.01200	.7000E-05
7	JP 2	1	.0128	.0139	.0133	.01333	.3033E-06
8	JP 3	1	.0141	.0143	.0150	.01447	.2233E-06
9	JP 4	1	.0117	.0125	.0129	.01237	.3733E-06
10	JP 5	1	.0140	.0150	.0180	.01567	.4333E-05
11	JP 6	1	.0133	.0133	.0130	.01320	.3000E-07
12	NL 1	1	.0124	.0127	.0119	.01233	.1633E-06
13	SW 1	1	.0170	.0150	.0140	.01533	.2333E-05
14	SW 2	1	.0140	.0160	.0140	.01467	.1333E-05

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-2 (USINOR KDF)

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	30.790
CHI-SQUARE(.95,13)	22.367

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

NONE REJECTED

DIXON'S TEST FOR LABORATORY MEANS

LAB- 3 R = .800 D-CRIT(14) = .586

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 3 DIXON'S TEST FOR LABORATORY MEANS

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-2 (USINOR KDF)

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	12	.63169744E-04	.52641453E-05
WITHIN LABS	26	.35340000E-04	.13592308E-05
TOTAL	38	.98509744E-04	

REPEATABILITY VARIANCE	.13592308E-05
REPEATABILITY STD. DEV.	.00116586
BETWEEN-LABORATORIES VARIANCE	.13016382E-05
BETWEEN-LABORATORIES STD. DEV.	.00114089
REPEATABILITY	.00329939
PERMISSIBLE TOLERANCE BETWEEN LABS	.00398342
GRAND MEAN	.01369744
VARIANCE OF THE GRAND MEAN	.13497808E-06

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-3 (MALMBERGET CONC)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS			LAB MEAN	LAB VARIANCE
1	AU 1	1	.1830	.1830	.1850	.18367	.1333E-05
2	AU 2	1	.1580	.1620	.1710	.16367	.4433E-04
3	AU 3	1	.2400	.2560	.2910	.26233	.6803E-03
4	AU 4	1	.1720	.1820	.1760	.17667	.2533E-04
5	AU 5	1	.1760	.1840	.1980	.18600	.1240E-03
6	JP 1	1	.1700	.1700	.1600	.16667	.3333E-04
7	JP 2	1	.1665	.1610	.1610	.16283	.1008E-04
8	JP 3	1	.1708	.1818	.1855	.17937	.5846E-04
9	JP 4	1	.1887	.1832	.1873	.18640	.8170E-05
10	JP 5	1	.1610	.1770	.1770	.17167	.8533E-04
11	JP 6	1	.1720	.1747	.1748	.17383	.2523E-05
12	NL 1	1	.1730	.1680	.1690	.17000	.7000E-05
13	SW 1	1	.1900	.1900	.1800	.18667	.3333E-04
14	SW 2	1	.1900	.1800	.1700	.18000	.1000E-03

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-3 (MALMBERGET CONC)

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	27.832
CHI-SQUARE(.95,13)	22.367

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

LAB- 3 C-CALC = .561 C-CRIT(3,14) = .351

DIXON'S TEST FOR LABORATORY MEANS

LAB- 3 R = .794 D-CRIT(14) = .586

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 3 DIXON'S TEST FOR LABORATORY MEANS

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-3 (MALMBERGET CONC)

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	12	.26415759E-02	.22013132E-03
WITHIN LABS	26	.10664800E-02	.41018462E-04
TOTAL	38	.37080559E-02	

REPEATABILITY VARIANCE	.41018462E-04
REPEATABILITY STD. DEV.	.00640457
BETWEEN-LABORATORIES VARIANCE	.59704288E-04
BETWEEN-LABORATORIES STD. DEV.	.00772685
REPEATABILITY	.01812492
PERMISSIBLE TOLERANCE BETWEEN LABS	.02534605
GRAND MEAN	.17595641
VARIANCE OF THE GRAND MEAN	.56443929E-05

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-4 (MALMBERGET CONC)

LABORATORY NO.	COUNTRY	BOTTLE NO.	ANALYTICAL RESULTS			LAB MEAN	LAB VARIANCE
1	AU 1	1	.8830	.9060	.9220	.90367	.3843E-03
2	AU 2	1	.8390	.8270	.8480	.83800	.1110E-03
3	AU 3	1	1.1100	1.1600	1.1300	1.13333	.6333E-03
4	AU 4	1	1.0000	1.0800	1.0500	1.04333	.1633E-02
5	AU 5	1	.9270	.9540	1.0300	.97033	.2852E-02
6	JP 1	1	.8300	.8600	.8700	.85333	.4333E-03
7	JP 2	1	.6105	.6105	.5966	.60587	.6440E-04
8	JP 3	1	.7988	.7850	.7817	.78850	.8229E-04
9	JP 4	1	.8464	.8380	.9296	.87133	.2564E-02
10	JP 5	1	.8730	.8860	.8730	.87733	.5633E-04
11	JP 6	1	.8878	.9296	.8877	.90170	.5838E-03
12	NL 1	1	.8820	.8810	.8790	.88067	.2333E-05
13	SW 1	1	.8900	.9000	.9300	.90667	.4333E-03
14	SW 2	1	.8200	.8600	.8200	.83333	.5333E-03

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-4 (MALMBERGET CONC)

BARTLETT'S TEST FOR HOMOGENEITY OF LABORATORY VARIANCE

CALCULATED STATISTIC	23.659
CHI-SQUARE(.95,13)	22.367

VARIANCE IS INHOMOGENEOUS

COCHRAN'S TEST FOR LABORATORY VARIANCE

NONE REJECTED

DIXON'S TEST FOR LABORATORY MEANS

LAB- 7 R = .624 D-CRIT(14) = .586

LIST OF LABORATORIES WHOSE RESULTS WERE NOT USED FOR ONE-WAY ANOVA

LAB- 7 DIXON'S TEST FOR LABORATORY MEANS

LIST OF INDIVIDUAL OUTLIERS DETECTED BY DIXON'S TEST WITHIN-LABORATORIES

NONE REJECTED

ISO/TC 102/SC 2/WG 22A - WATER SOLUBLE CHLORIDE
SAMPLE: 82-4 (MALMBERGET CONC)

ONE-WAY ANALYSIS OF VARIANCE TABLE

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARE
BETWEEN LABS	12	.31143375E+00	.25952812E-01
WITHIN LABS	26	.20605987E-01	.79253795E-03
TOTAL	38	.33203974E+00	

REPEATABILITY VARIANCE	.79253795E-03
REPEATABILITY STD. DEV.	.02815205
BETWEEN-LABORATORIES VARIANCE	.83867582E-02
BETWEEN-LABORATORIES STD. DEV.	.09157925
REPEATABILITY	.07967030
PERMISSIBLE TOLERANCE BETWEEN LABS	.26522139
GRAND MEAN	.90781026
VARIANCE OF THE GRAND MEAN	.66545673E-03